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A fluorescent coating.

A method for improving the optical performance of fluorescent coatings by the use of hollow polymer particles which scatter ultraviolet light and shorter wavelength visible light is described. The hollow polymer particles may be employed as an additive in a fluorescent coating, as an additive in a basecoat composition onto which a conventional fluorescent coating composition is applied, or as an additive in both the fluorescent coating composition and the basecoat composition onto which the fluorescent coating composition is applied.

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The present invention relates to a fluorescent coating.

In particular, the present invention relates to a fluorescent coating comprising hollow polymer particles which scatter ultraviolet light and shorter wavelength visible light. The present invention also relates to a method for improving the appearance of fluorescent coatings through the use of such hollow polymer particles.

The term "coating" as used herein includes single layer coatings and multilayer coatings such as those consisting of a basecoat made from a basecoat composition and an over-laying coating layer made from a coating composition.

The term "fluorescent coatings" as used herein are coatings which contain a fluorescent additive, such as pigment and dye, and include but are not limited to paints, inks, leather coatings, adhesives, films and the like.

Fluorescent coatings (e.g. fluorescent paints and inks) are aesthetically desirable in certain applications such as, for example, where safety or decorative purposes are important because of the high degree of visibility generated by the intensity of the fluorescent pigment colours. These fluorescent pigments exhibit their bright colours under daylight conditions as well as under fluorescent and mercury lamps. The appearance of fluorescent coatings is the result of the absorption and re-emission of light by the fluorescing pigment.

A problem associated with fluorescent coatings has been their poor covering power. In this regard, light tends to pass through the fluorescent coatings and is absorbed by the substrate reducing the brightness of the coated article.

Conventional light scattering pigments, such as for example, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, kaolin and lithopone can increase the covering or hiding power of coatings. However, when such pigments are incorporated into fluorescent coatings the added whiteness only detracts from the desired high chroma of the fluorescent coating.

One proposed solution to this problem has been the application onto the substrate of a first opaque coating or basecoat onto which the fluorescent coating can subsequently be applied or printed. This solution, however, increases the number of steps and coatings necessary to achieve the desired appearance.

One example of this approach can be found in JP-A-63131637 which teaches the use of hollow glass powders or glass balloons in a fluorescent paint or ink. The hollow glass powders are incorporated into the fluorescent paint at a concentration of from about 5% to 20 % by weight and have an average particle size diameter of about 20 microns to 50 microns and a wall thickness of several microns. Apparently, fluorescent paints containing these hollow glass powders can eliminate the need for a white basecoat.

Another example can be found in GB-A-2224737 which teaches a water-based ink composition for writing on neon boards comprising at least 30% by weight water; 0.5-50% by weight hollow resin particles; 0.5-30% by weight resin which is film-forming at room temperature; and 0.5-25% dry weight of aqueous emulsion of at least one nonvolatile or only slightly volatile liquid selected from aliphatic carboxylic acid esters, higher hydrocarbons and higher alcohols. Markings from this ink composition on transparent glass or plastic panels are intensely brightened when a surface receives incident light perpendicular into the panel.

It is an object of the invention to improve the fluorescence of fluorescent coatings, such as paints and inks.

According to a first aspect of the present invention there is provided a coating comprising at least one hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light; and at least one fluorescent additive which absorbs light and fluoresces the light.

According to a second aspect of the present invention there is provided the use of at least one hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light in a coating comprising at least one fluorescent additive for enhancing the fluorescence of the coating.

According to a third aspect of the present invention there is provided an article coated with a coating according to the first aspect of the present invention.

In one preferred embodiment, the coating comprises a basecoat composition and a coating composition wherein either the basecoat composition or the coating composition comprises the at least one hollow polymer particle.

In another preferred embodiment, the coating comprises a basecoat composition and a coating composition wherein either the basecoat composition or the coating composition comprises the at least one fluorescent additive.

In one embodiment, the at least one hollow polymer particle and the at least one fluorescent additive may both be present in the coating composition. In another embodiment, the at least one hollow polymer particle may be present in the basecoat composition and the at least one fluorescent additive may be present in the coating composition.

In another embodiment, both the coating composition and the basecoat composition may comprise the at least one hollow polymer particle and the at least one fluorescent additive.

Preferably, the hollow polymer particle comprises from about 1% by weight to about 90% by weight of the coating composition solids, basecoat solids or total coating solids. More preferably, the hollow polymer particle

comprises from about 5% by weight to about 50% by weight of the coating composition solids, basecoat solids or total coating solids.

Advantageously, the hollow polymer particles have a particle size diameter of from about 0.07 microns to about 4.5 microns and a void diameter of from about 0.05 microns to about 3.0 microns. Preferably, the hollow polymer particles have a particle size diameter of from about 0.1 micron to about 3.5 microns.

Preferably the coating is either a paint or an ink.

Preferably, the at least one fluorescent additive absorbs light with a wavelength less than about 500 nanometers.

Preferably, the fluorescent additive is orange, yellow, red, blue, green, pyranine, fluorescein, or Rhodamine B pigment.

Conventional coating components such as, for example, pigments, binders, vehicles, extenders, dispersants, surfactants, coalescents, wetting agents, rheology modifiers, thickeners, drying retarders, antifoaming agents, colorants, waxes, preservatives, heat stabilizers, solvents, anti-skinning agents, driers and the like may be used in the coatings of the present invention.

The present invention therefore provides a method for improving the fluorescence of a coating composition containing at least one fluorescent additive comprising adding to the coating composition at least one type of hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light in an effective amount to enhance the fluorescence of the coating composition.

The present invention also provides a method for improving the fluorescence of a coating comprising a basecoat composition and a coating composition containing at least one fluorescent additive, the method comprising adding to the basecoat composition at least one type of hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light in an effective amount to enhance the fluorescence of the coating composition.

The present invention also provides a basecoat composition for a coating which comprises at least one fluorescent additive which absorbs light with a wavelength less than about 500 nanometers and fluoresces the light, wherein the basecoat comprises at least one hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light.

The present invention may therefore be practiced by:

1. adding the hollow polymer particles directly into the fluorescent coating;
2. adding the hollow polymer particles into a basecoat for the substrate onto which is subsequently applied a conventional fluorescent coating; or
3. adding the hollow polymer particles into both the basecoat and conventional fluorescent coating.

Incorporation of the hollow polymer particles directly into the fluorescent coating eliminates the need for additional coatings to obtain good opacity and fluorescence.

The utilisation of the hollow polymer particle according to the present invention (i.e. hollow polymer particles which do not substantially absorb near ultraviolet light and shorter wavelength visible light) improves the fluorescence of coatings. As it has been made clear, the hollow polymer particle may be employed as an additive in a fluorescent coating, as an additive in a basecoat onto which a conventional fluorescent coating is applied, or as an additive in both a fluorescent coating and a basecoat onto which the fluorescent coating is applied.

The hollow polymer particles may also be added to obtain the enhanced fluorescent effect in other materials, such as plastics and other molded articles, which utilize fluorescent additives.

A number of publications describing hollow polymer particles are known. These publications include US-A-3,784,391; US-A-4,427,836; US-A-4,469,825; US-A-4,594,363; US-A-4,880,842; US-A-4,829,102; J. W. Hook and R. E. Harren, "Opaque Polymers," *Organic Coatings - Science and Technology*, Volume 7 (New York: Marcel Dekker, Inc., 1984), pp. 299-315; J. W. Hook *et al.*, "Wet Hiding in Paints Containing Opaque Polymer Modifiers," *Resin Review*, XXXVI, No. 3, 3-7 (1986); D. M. Fasano *et al.*, "Formulating High PVC Paints with Opaque Polymer Additives," *Resin Review*, XXXVII, No. 2, 21-31 (1987); J. T. Brown *et al.*, "Gaining an Edge in Coating Publication Papers," *Resin Review*, XXXVII, No. 2, 14-19 (1987); W. J. Gozdan *et al.*, "Confirming the Exterior Durability of Ropaque® OP-62 Opaque Polymer," *Resin Review*, XXXIX, No. 2, 15-24 (1987); and D.M. Fasano, "Use of Small Polymeric Microvoids in Formulating High PVC Paints," *J. Coat. Tech.*, 59, NO. 752, 109-116 (September 1987).

The hollow polymer particles which are useful in this invention may be made in accordance with, and having the properties disclosed in, the teachings of US-A-3,784,391, US-A-4,798,691, US-A-4,908,271, US-A-4,910,229, US-A-4,972,000, JP-A-60/223873, JP-A-61/62510, JP-A-61/66710, JP-A-61/86941, JP-A-62/127336, JP-A-62/156387, JP-A-01/185311 and JP-A-02/140272. The preferred hollow polymer particles and their method of manufacture are disclosed in US-A-4,427,836, US-A-4,469,825, US-A-4,594,363 and US-A-4,880,842.

While the hollow polymer particles according to the present invention provide hiding or covering power to coatings in much the same manner as opacifying pigments, such as for example titanium dioxide (TiO₂) and zinc oxide, they also exhibit a significantly different behavior when a coating containing them is exposed to ultraviolet light (UV). However, unlike conventional opacifying pigments, the hollow polymer particles of the present invention do not substantially absorb light which normally excites fluorescent pigments, such as ultraviolet light and shorter wavelength visible light. As a result of this phenomenon the hollow polymer particles of the present invention both permit a greater flux of ultraviolet light and shorter wavelength visible light in a coating and, in the case of a coating which contains a fluorescent additive, improve the fluorescence of the coating compared with conventional opacifying pigments.

Under light of visible wavelengths, fluorescent paints formulated with titanium dioxide as an opacifying pigment and paints formulated with hollow polymer particles at concentrations designed to match the visible light scattering of the conventional paint are visually similar. However, when these paint films are placed under ultraviolet light illumination, the paints formulated with the hollow polymer particles exhibit a much higher degree of fluorescence.

In addition, the phenomenon is applicable with any fluorescent additive, such as for example pigments and dyes, which are initially excited by ultraviolet light and visible light with a wavelength less than about 500 nanometers (nm), preferably less than about 450 nanometers. The fluorescent pigments and dyes which exhibit this effect in coatings containing the hollow polymer particles include, for example, DayGlo™ Saturn Yellow, DayGlo™ Rocket Red, DayGlo™ Horizon Blue, pyranine, fluorescein, Rhodamine B and the like. (DayGlo is a trademark of the DayGlo Corporation).

The hollow polymer particles according to the present invention are useful in fluorescent coatings at levels of from about 1% by weight to about 90% by weight of the formulation solids. Generally, levels of less than about 1% by weight of the formulation solids do not provide sufficient opacity. Generally, levels greater than about 90% by weight of the formulation solids interfere with film formation. Levels of hollow polymer particles from about 5% by weight to about 50% by weight of the formulation solids are preferred.

The hollow polymer particles useful in fluorescent coatings have particle size diameters of from about 0.07 microns to about 4.5 microns, preferably from about 0.1 microns to about 3.5 microns. Hollow polymer particles with a void diameter of from about 0.05 microns to about 3.0 microns are preferred.

The present invention will now be described by way of examples only.

Fluorescence Measurement

In the following Examples, the analysis was performed on small pieces (1 cm x 2 cm) cut from the black portion of a opacity chart for the fluorescent paint coatings. Analysis was performed on a black vinyl chart for the basecoat paint coatings.

Fluorescence spectra of the paint specimens were obtained using Spex Fluorolog II® Spectrofluorometer used in conjunction with a Spex Model DM1B Data Analyzer. A 150 Watt Xenon lamp was used for the excitation source for ultraviolet and visible wavelength regions. Steady state emission spectra were obtained by holding the excitation wavelength constant while scanning the emission at longer wavelengths. Emitted light was detected using a photomultiplier with an operating voltage of -900 volts and a Spex Model DM102 Photon Counting Acquisition Module. The intensity (measured in photons per second) was recorded at intervals of 0.5 nanometers. Paint specimens were examined using front face illumination: the exciting light impinged upon the paint squares at an angle roughly 45° to the normal of the sample surface, and the signal was collected at 22° relative to the excitation source. Slits were varied between sample sets from 0.5 mm to 1.25 mm as necessary such that the detected signal was kept in the linear range of the photomultiplier tube response.

A steady state emission spectrum was collected for each paint sample using an ultraviolet and visible wavelength. From each spectrum, the wavelength at which the maximum intensity occurred and the corresponding intensity at this wavelength (I_{\max}) was determined. Data were collected successively in pairs, with each pair consisting of the hollow polymer particle paint (basecoat or fluorescent coating) and its TiO₂ control.

The reported fluorescence enhancement is computed as the ratio of the measured maximum intensity of the hollow polymer particle paints samples to the maximum intensity of the TiO₂ controls at the same maximum wavelength: $I_{\max(\text{hollow polymer})}/I_{\max(\text{TiO}_2)}$. This intensity ratio was measured for both ultraviolet excitation (375 nm) and visible excitation (500 nm). These wavelengths were chosen as typical for the spectral regions of interest.

Example 1. Preparation of Paint Formulations without Colourants

Three types of paints were initially formulated:

FORMULATION 1: Paint containing only hollow polymer particles as opacifying pigment

FORMULATION 2: Paint containing only titanium dioxide (TiO₂) as opacifying pigment (COMPARATIVE)

FORMULATION 3: Paint containing no hollow polymer particles or titanium dioxide (TiO₂) as opacifying pigment (COMPARATIVE)

[Note: All quantities of ingredients are listed in Table 1.1.]

To a 0.57 litre (1 pint) plastic paint can equipped with a laboratory stirrer, an acrylic latex was added. At moderate agitation, a polycarboxylic acid dispersant was added and mixed. Then the opacifying pigment (either predispersed TiO₂ slurry or hollow polymer particles) was added and mixed. Finally water was added and the paint formulation was mixed for an additional 15 minutes.

Table 1.1

NOTE: All quantities in grams

	FORMULATION		
	1	2 Comparative	3 Comparative
Acrylic latex (Rhoplex® AC-382) (51.8% total solids)	349.8	424.1	437.2
Polycarboxylic acid dispersant (Tamol® 963) (35% total solids)	1.0	1.0	1.0
TiO ₂ slurry (Ti-Pure® R-900) (76.5% total solids)	--	31.7	--
Hollow polymer particles (Ropaque® OP-62) (37.5% total solids)	79.8	--	--
Water 1.93	7.3	0.8	

Example 2. Preparation of Paint Formulations with Equal Opacity

In order to approximately match the opacity of the formulation containing hollow polymer particles to the formulation containing TiO₂, blends of Formulation 2 (TiO₂-containing) and Formulation 3 (no TiO₂ or hollow polymer particles) were made to 1/2, 1/3 and 1/6 of the TiO₂ level of Formulation 2 (see Table 2.1).

Formulations 2, 3, 4, 5 and 6 were drawn down side by side with Formulation 1 to minimize film thickness differences with a 17.78 x 10⁻² mm (7 mil) Dow bar on Leneta 5C opacity charts and dried at 50% relative humidity and 21.1°C (70°F) overnight.

Contrast ratios were determined by the ratio of the reflectance of each coating over the black portion of the opacity chart to the reflectance of each coating over the white portion of the opacity chart as measured by a Pacific Scientific Colorgard® 45°/0° Reflectometer. Relative contrast ratios were then determined by the ratio of the contrast ratio of the comparative paints (Comparative Formulations 2-6) to the contrast ratio of Formulation 1. The results are also reported in Table 2.1.

Table 2.1

	Formulation	Level of TiO ₂ Slurry (weight %)	Level of Formulation 2 (grams)	Level of Formulation 3 (grams)	Relative Contrast Ratio
5					
10	1	0.0	0.0	0.0	1.000 (by definition)
	2	6.93	45.0	0.0	1.333
	3	0.0	0.0	45.0	0.157
15	4*	3.53	22.88	22.01	1.114
	5**	2.37	15.25	29.34	0.934
	6***	1.19	7.63	36.68	0.581
20	NOTES: * Formulation 4 contains 1/2 the TiO ₂ of Formulation 2 ** Formulation 5 contains 1/3 the TiO ₂ of Formulation 2 *** Formulation 6 contains 1/6 the TiO ₂ of Formulation 2				

The TiO₂ level at which the plot of the relative contrast ratio versus TiO₂ level for Comparative Formulations 2-6 equals unity (1.000) is the point of approximately equal opacity between Formulation 1 (containing only hollow particles) and a formulation containing TiO₂. This point corresponds to a level of 2.70 weight % TiO₂ slurry. In order to obtain a paint formulation with the necessary TiO₂ level, 156.5 grams of Comparative Formulation 2 and 245.6 grams of Comparative Formulation 3 were blended to give COMPARATIVE FORMULATION 7 (no hollow polymer particles).

Example 3. Preparation of Paint Formulations with Colourants (Topcoat Paint)

Colorants were added to equal volume aliquots of Formulation 1 and Formulation 7 according to levels in Table 3.1.

Table 3.1

NOTE: H – contains hollow polymer particles
T – contains TiO₂

	Formulation	Weight of Formulation (grams)	Colorant	Weight of Colorant (grams)
Fluorescent Paint 1H	1	21.9	DayGlo™ Fire Orange	1.0001 ^a
Fluorescent Paint 1T Control	7	22.3	DayGlo™ Fire Orange	1.0001 ^a
Fluorescent Paint 2H	1	21.9	DayGlo™ Saturn Yellow	1.0000
Fluorescent Paint 2T Control	7	22.3	DayGlo™ Saturn Yellow	1.0000
Fluorescent Paint 3H	1	21.9	DayGlo™ Rocket Red	1.0000
Fluorescent Paint 3T Control	7	22.3	DayGlo™ Rocket Red	1.0000
Fluorescent Paint 4H	1	21.9	DayGlo™ Horizon Blue	1.0000
Fluorescent Paint 4T Control	7	22.3	DayGlo™ Horizon Blue	1.0000
Fluorescent Paint 5H	1	21.9	Pyranine	0.1051
Fluorescent Paint 5T Control	7	22.3	Pyranine	0.1051
Fluorescent Paint 6H	1	21.9	Fluorescein	0.1666
Fluorescent Paint 6T Control	7	22.3	Fluorescein	0.1666
Fluorescent Paint 7H	1	21.9	Rhodamine B	0.0797
Fluorescent Paint 7T Control	7	22.3	Rhodamine B	0.0797
Comparative Paint 8H	1	21.9	Acid Fuchsin	0.2126
Comparative Paint 8T Control	7	22.3	Acid Fuchsin	0.2126
Comparative Paint 9H	1	21.9	Cal-Ink Lamp Black	0.54
Comparative Paint 9T Control	7	22.3	Cal-Ink Lamp Black	0.54
Comparative Paint 10H	1	21.9	Cal-Ink Phthalo Blue	1.09
Comparative Paint 10T Control	7	22.3	Cal-Ink Phthalo Blue	1.09

^aDispersion of 4.0 g DayGlo™ Fire Orange/10.0 g H₂O/0.10 g Triton® X-100

Example 4. Preparation of Paint Formulations with Colourants (Basecoat Paint)

Formulations 1 and 7 were each drawn down several times with a wire wound rod on black vinyl opacity charts to build a thick layer of paint to ensure good opacity. The draw downs were dried at 50% relative humidity and 21.1°C (70°F) overnight. Both formulations were then coated with commercial fluorescent paints using a 17.78 x 10⁻²mm (7 mil) Dow bar. See Table 4.1. The drawdowns were then dried at 50% relative humidity and 21.1°C (70°F) overnight.

Table 4.1

5	NOTE:	H	--	contains hollow polymer particles
		T	--	contains TiO ₂
10	Coating/Basecoat System	Basecoat Formulation	Coating Fluorescent Paint	
	Fluorescent Paint 11H	1	DEKA Permanent Fabric Paint #491 Fluorescent Yellow	
	Fluorescent Paint 11T Control	7	DEKA Permanent Fabric Paint #491 Fluorescent Yellow	
15	Fluorescent Paint 12H	1	DEKA Permanent Fabric Paint #492 Fluorescent Orange	
	Fluorescent Paint 12T Control	7	DEKA Permanent Fabric Paint #492 Fluorescent Orange	
20	Fluorescent Paint 13H	1	DEKA Permanent Fabric Paint #494 Fluorescent Red	
	Fluorescent Paint 13T Control	7	DEKA Permanent Fabric Paint #494 Fluorescent Red	
	Fluorescent Paint 14H	1	DEKA Permanent Fabric Paint #495 Fluorescent Blue	
25	Fluorescent Paint 14T Control	7	DEKA Permanent Fabric Paint #495 Fluorescent Blue	
	Fluorescent Paint 15H	1	DEKA Permanent Fabric Paint #496 Fluorescent Green	
30	Fluorescent Paint 15T Control	7	DEKA Permanent Fabric Paint #496 Fluorescent Green	

Example 5. Preparation of Ink Formulations

All quantities of ingredients are listed in Table 5.1.

To a container equipped with a laboratory stirrer, the styren-acrylic alkali-soluble resin neutralized with ammonia was added.

At moderate agitation, the predispersed fluorescent pigment and then the emulsified wax were added and mixed. Then the opacifying pigment (either predispersed TiO₂ slurry or hollow polymer particles) was added and mixed. Finally water was added and the fluorescent ink was mixed for an additional 15 minutes.

Each fluorescent ink containing hollow polymer particles was drawn down with a #6 wire wound rod on coated clay, bleached white sealed paper and Kraft paper side-by-side with its respective TiO₂ control fluorescent ink.

The draw downs were dried with a heat gun for 10 seconds. (See Table 5.2.)

Table 5.1

NOTE: H – contains hollow polymer particles
T – contains TiO₂

	Fluorescent Ink 1	Fluorescent Ink 1 Control	Fluorescent Ink 2	Fluorescent Ink 2 Control
Styrene-acrylic alkali soluble resin binder neutralized with ammonia (18% solids)	45.7 grams	46.1 grams	44.7 grams	47.1 grams
Pigment Type	DAY-GLO™ Rocket Red	DAY-GLO™ Rocket Red	DAY-GLO™ Saturn Yellow	DAY-GLO™ Saturn Yellow
Pigment Level (50% solids)	35.4 grams	37.0 grams	34.7 grams	38.0 grams
Jonwax® 26 Emulsified Wax	5.9 grams	5.9 grams	5.7 grams	6.0 grams
Ropaque® OP-62 (37.5% solids)	6.3 grams	–	6.4 grams	–
Flexiverse® Predispersed TiO ₂ (72% solids)	–	2.8 grams	–	2.7 grams
Water	6.6 grams	8.2 grams	8.6 grams	6.3 grams
% Total Solids	30.0	30.0	29.3	31.2
% Pigment	17.7	18.5	17.35	19.0

Table 5.2

NOTE: H – contains hollow polymer particles
 T – contains TiO_2
 A – clay coated paper
 B – bleached white sealed paper
 C – Kraft paper

	Ink	Opacifier	Type of Paper
Fluorescent Ink 1A-H	Red	Hollow polymer particles	Clay
Fluorescent Ink 1A-T Control	Red	TiO_2	Clay
Fluorescent Ink 1B-H	Red	Hollow polymer particles	Sealed
Fluorescent Ink 1B-T Control	Red	TiO_2	Sealed
Fluorescent Ink 1C-H	Red	Hollow polymer particles	Kraft
Fluorescent Ink 1C-T Control	Red	TiO_2	Kraft
Fluorescent Ink 2A-H	Yellow	Hollow polymer particles	Clay
Fluorescent Ink 2A-T Control	Yellow	TiO_2	Clay
Fluorescent Ink 2B-H	Yellow	Hollow polymer particles	Sealed
Fluorescent Ink 2B-T Control	Yellow	TiO_2	Sealed
Fluorescent Ink 2C-H	Yellow	Hollow polymer particles	Kraft
Fluorescent Ink 2C-T Control	Yellow	TiO_2	Kraft

Example 6. Fluorescence Measurement

The fluorescence measurements were made as previously described. The results are reported in Table 6.1 for the fluorescent coating paints, in Table 6.2 for the basecoat paints and in Table 6.3 for the fluorescent inks.

Table 6.1

$I_{\max}(\text{hollow polymer})/I_{\max}(\text{TiO}_2)$			
	UV (375 nm)	Visible (500 nm)	Maximum Emission Wavelength (nm)
Fluorescent Paint 1	5.7	0.9	594
Repeat	4.8	—	594
Repeat	6.3	—	594
Repeat*	5.7	0.9	594
Fluorescent Paint 2*	5.7	1.0	510
Fluorescent Paint 3*	5.0	0.9	595
Fluorescent Paint 4*	4.9	—	434
Fluorescent Paint 5	2.1	—	434
Fluorescent Paint 6	4.6	1.0	520
Repeat	3.8	—	520
Fluorescent Paint 7	3.0	0.8	611
Comparative Paint 8	1.2 (428 nm) 1.5 (635 nm)	— 0.8 (635 nm) 0.8 (650 nm)	— — —
Comparative Paint 9	1.3	—	428
Comparative Paint 10	1.2	—	428
Formulation 1/Formulation 7 (Control)	1.8	—	428
Repeat*	1.8	—	428

*NOTE: Kubelka-Munk scattering coefficients were determined for Formulations 1 and Comparative Formulations 2-6 to verify that Formulation 1 and Comparative Formulation 7 were of approximately equal opacity. This analysis predicted that 2.77 weight % TiO_2 slurry was needed in Comparative Formulation 7 to match the opacity of Formulation 1. This value was used in these formulations and is believed to be essentially equivalent to the formulations with 2.70 weight % TiO_2 .

Table 6.2

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10

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Table 6.3

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$I_{\max}(\text{hollow polymer})/I_{\max}(\text{TiO}_2)$			
	UV (375 nm)	Visible (500 nm)	Maximum Emission Wavelength (nm)
Fluorescent Paint 11	1.6	1.2	520
Fluorescent Paint 12	1.6	1.2	603
Fluorescent Paint 13	1.6	1.0	608
Repeat	1.3	—	608
Fluorescent Paint 14	1.1	—	444
Repeat	1.1	—	444
Fluorescent Paint 15	0.9	0.8	510
Repeat	1.3	—	510

$I_{\max}(\text{hollow polymer})/I_{\max}(\text{TiO}_2)$		
	UV (375 nm)	Visible (500 nm)
Fluorescent Ink 1A	1.8	1.0
Fluorescent Ink 1B	1.6	1.1
Fluorescent Ink 1C	1.1	0.8
Fluorescent Ink 2A*	0.3	0.2
Fluorescent Ink 2B	1.4	1.0
Fluorescent Ink 2C	1.2	1.0

*This value may be the result of the contribution of the rough paper surface to the detected signal and the limited opacity of the yellow ink. Repeat measurements confirmed values less than 1.

In Table 6.1, I_{\max} ratios greater than 1.8 (Control) indicate enhanced fluorescence.
In Table 6.2, I_{\max} ratios greater than 1.0 (Control) indicate enhanced fluorescence.

In Table 6.3, I_{\max} ratios greater than 1.0 indicate enhanced fluorescence.

Claims

1. A coating comprising
 - at least one hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light; and
 - at least one fluorescent additive which absorbs light and fluoresces the light.
2. A coating according to claim 1 comprising a basecoat composition and a coating composition wherein either the basecoat composition or the coating composition comprises the at least one hollow polymer particle.
3. A coating according to claim 1 or claim 2 comprising a basecoat composition and a coating composition wherein either the basecoat composition or the coating composition comprises the least one fluorescent additive.
4. A coating according to any one of claims 1 to 3 wherein the hollow polymer particle comprises from about 1 % by weight to about 90% by weight of the coating composition solids, basecoat solids or total coating solids.
5. A coating according to any one of claims 1 to 4 wherein the at least one hollow polymer particle has a particle size diameter of from about 0.07 microns to about 4.5 microns and a void diameter of from about 0.05 microns to about 3.0 microns.
6. A coating according to any one of claims 1 to 5 wherein the at least one fluorescent additive absorbs light with a wavelength less than about 500 nanometers.
7. An article coated with a coating according to any one of claims 1 to 6.
8. The use of at least one hollow polymer particle which scatters ultraviolet light and shorter wavelength visible light in a coating for enhancing the fluorescence of the coating.



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⑤④ **A fluorescent coating.**

⑤⑦ A method for improving the optical performance of fluorescent coatings by the use of hollow polymer particles which scatter ultraviolet light and shorter wavelength visible light is described. The hollow polymer particles may be employed as an additive in a fluorescent coating, as an additive in a basecoat composition onto which a conventional fluorescent coating composition is applied, or as an additive in both the fluorescent coating composition and the basecoat composition onto which the fluorescent coating composition is applied.

EP 0 497 507 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0594

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, A	GB-A-2 224 737 (SAKURA COLOR PRODUCTS CORPORATION) ---	1	C09D5/00 C09D7/12 C09D11/00
A	EP-A-0. 267 726 (ROHM AND HAAS COMPANY) * abstract * * claims 1,8,9 *	1,8	
A	US-A-4 324 682 (NORMA A.WESTON ET AL) ---	1-8	
A	DATABASE WPIL Week 0390, Derwent Publications Ltd., London, GB; AN 90020335 & JP-A-1 301 767 (DAINIPPON TORYO KK) 5 December 1989 * abstract *	1	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 FEBRUARY 1993	Examiner CATURLA VICENTE V.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

EPO FORM 1501 (12/92) (P0401)